INDIAN HEAD DIVISION
NAVAL SURFACE WARFARE CENTER
INDIAN HEAD, MD

Erratum to

IHTR 2375

DECONTAMINATION METHODS FOR AMMONIUM PERCHLORATE CONTAMINATED BUILDINGS AND EQUIPMENT SURFACES

Dated 30 September 2001

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FOREWORD

This work was performed at the Indian Head Division, Naval Surface Warfare Center, Indian Head, MD.

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INTRODUCTION

Background

Ammonium perchlorate (AP) has been extensively used as one of nine major components of propellant, explosive, and pyrotechnic materials for decades. Most, if not all, of the processes discharge AP wastes into the environment, both in soils and water. AP is quite pervasive owing to its high water solubility and transport by all water media, both surface and subsurface.

It is incumbent then on the industry to develop clean-up techniques that will remove the AP contaminant to the non-detectable level using present laboratory techniques. To assist in identifying the methods that might be used to remove AP from the contaminated surfaces, an extensive literature search was performed. Once candidate reactions were identified, they were tested under laboratory conditions for the selection of the optimum technique.

Approach

1. Search the Internet and scientific journals for literature citing reactions of AP and selected reagents that reduce AP to its chloride.

2. Obtain and study the literature identified. Select the reaction that will yield the most benign environmental by-products while reducing the AP to acceptable (EPA) levels.

3. Prepare appropriate solutions of AP and reagents and conduct laboratory reactions to confirm findings of the literature search.

4. Report all findings.

FINDINGS

Literature Search

A search of the bibliographies available in the A.T. Camp Technical Library at the Indian Head Division identified three candidate publications. Inquiries to pertinent technical societies turned up two additional sources. The seeming dearth of applicable literature sources was owed to the stringent requirements that the candidate reagents had to meet:

- The reagents used to decompose the perchlorate would be environmentally benign.
- The products of the reaction of the perchlorate with the reactants would be environmentally benign.
- Optimal temperature for the reaction to occur would be at or slightly above ambient.
- The reaction would be sufficiently robust as to consume the perchlorate in a relatively brief period.
- The reactants would not be particularly aggressive to a variety of the surfaces anticipated to be treated.
- The reactants would not be hazardous to personnel (i.e., flammable, lachrymators, etc.).
- The physical qualities of the reactants would render them amenable to application with commonly used equipment (i.e., power sprayers).
- The reagents would be commercially available and relatively inexpensive.

The publications selected for review/study were:

1. Tofan, M.C.D. et al., "Reduction of Perchlorate by Titanous Ions in Ethanolic Solution." Submitted for publication August 1999.
2. Duke, F.R.; Quinney, P.D., "The Kinetics of Reduction of Perchlorate Ions by Ti (III) in Dilute Solution." *Journal of the American Chemical Society*, 1954, 76, 3800-3803.
3. Bredig and Michel., *Z. physik. Chem*., 100, 1245 (1922).
4. Basom K., "Analysis of Ammonium Perchlorate by Ion Chromatography." *JANNAF Proceedings*. 1993.
5. Basom K., Tinsley L., "Trace Analysis of Perchlorate in Environmental Matrices." Presentation at *5th Annual Joint Services Pollution Prevention and Hazardous Waste Management Conference*, August 2000.

Literature Review Results

Initial cursory review of the literature indicated that the reduction of the perchlorate has a favorable E° (oxidation potential) for reduction in an acidic medium (+1.19 volts). Reactions with common reductants incorporating divalent iron, chromate, and tin, however, had high activation energies and, consequently, low reaction rates. This was likely due to the chloride portion of the ion residing in the interior and the inability of the divalents to complex with the surrounding oxygen and expose the halogen. Titanous ion, however, is capable of reduction of the perchlorate. Recent work (per publication 1) has shown facile reduction of perchlorate in ethanolic solution. Reaction in an aqueous medium, however, is inhibited by the polarity of water, and the use of ethyl alcohol, a flammable solvent, in a decontamination protocol is problematic. Past work involving the reduction of perchlorate by trivalent titanium (per publications 2 and 3) describes the rapid reaction of perchlorate in an acidic medium. The reaction proceeds to completion, generating tetravalent titanium, chloride ion, and water. The reaction meets all of the above criteria—

- The reagents, titanium chloride and dilute acid, are environmentally benign.
- The products of the reaction, tetravalent titanium with chloride and water, are also environmentally benign.
- The reaction occurs at ambient temperature; however, slight elevations in temperature appear to facilitate reaction.
- The stated rates indicate a rapid reaction.
- The titanium and dilute acidic medium are not aggressive towards a wide variety of materials or hazardous to personnel.
- The properties of the materials allow for application to surfaces by commonly used means.
- Materials are readily available and relatively inexpensive.

Laboratory Confirmation of Literature Search

Solutions of all the reagents to be used were composed in the laboratory. Tests were conducted to determine reaction times as a function of perchlorate concentration, acid concentration, and temperatures. A suitable quenching agent, which will halt the reaction at desired intervals and not provide interference to the eventual quantitation of the perchlorate, was tested. The analyses described in publications 3 and 4 will detect perchlorate down to the parts to sub-parts per billion range to provide a measure of reaction completion. The latter is important since the original work is dated (1922 and 1954) and the completion of reaction was determined at concentrations above current acceptable levels for defining the absence of perchlorate ($\leq$1 part per million).

A study was conducted to evaluate titanium (III) chloride's ($TiCl_3$) potential for use as an agent to remove perchlorate from surfaces as part of decontamination protocols. Test solutions consisted of the titanous salt, a proton source (acetic acid), and concentrations of perchlorate ion ranging from approximately 370 parts per million (ppm) to 1,300 ppm. Solutions were allowed to react for 1 minute and 10 minutes before quenching. The composition of each solution is listed in Table I.

Table I. Compositions of Solutions

Solution No.	Perchlorate concentration (ppm)	Perchlorate concentration (molarity)	$TiCl_3$ (molarity)	H^+ (molarity)
1	370	0.003	0.6	0.1
2	700	0.007	0.6	0.1
3	1200	0.012	0.5	0.1

Previously composed solutions had contained perchlorate at <100 ppm. Due to the low concentration of the perchlorate and other reactants, the activity of the solutions proved insufficient for reaction. The quenching of the above solutions was, subsequently, effected by dilution of the solutions at the indicated time intervals rather than through the addition of a facile oxidizer (a cerium salt). All test solutions were analyzed by ion chromatography.

The results of the analyses are listed in Table II and depicted graphically in Figure 1. As can be seen, depletion of the perchlorate was observed in all three solutions. As depicted in the figure, the rate of reaction appeared to slow as the concentrations approached 100 to 200 ppm; in the case of solution 1, no further reaction of perchlorate was observed after the concentration dropped to 180 ppm. This phenomenon appears to be a product of the lowered activity that was previously observed in the dilute solutions. The rapid drop in concentration in solution 3 after 1 minute, followed by a decrease in rate could be accounted for by the consumption of the Ti (III) with a subsequent decrease in the solution's activity, the same phenomena likely responsible for the curve generated by solution 2.

Table II. Results of Analysis of Perchlorate Solutions Treated with Ti (III)

Time (min)	Perchlorate concentration (ppm)		
	Solution 1	Solution 2	Solution 3
0	350	700	1200
1	180	500	700
10	180	300	300

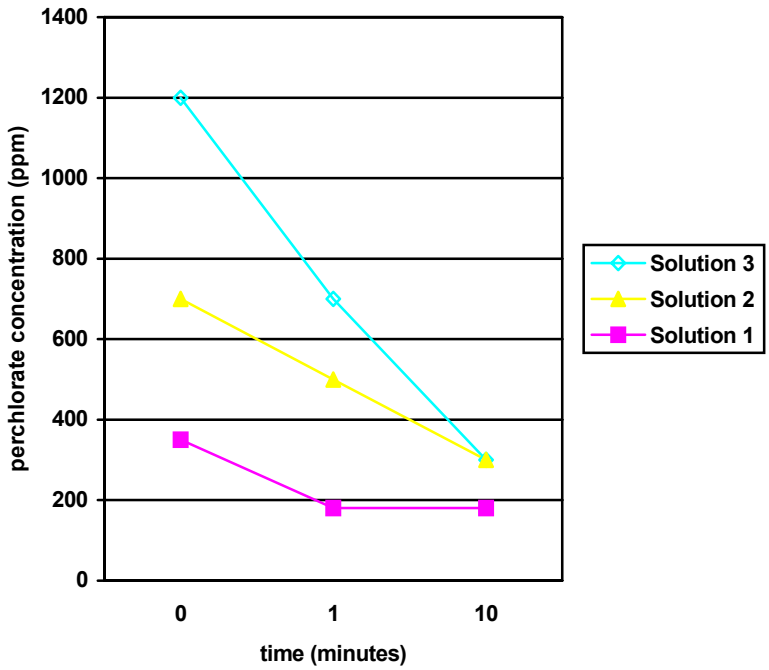

Figure 1. Reduction of Perchlorate Versus Concentration

An increase in rate and decrease in perchlorate below the observed level could be most readily effected by increasing the concentration of reactants or the kinetics of the system through elevation of temperature. While the kinetics of the system has been defined at higher concentrations (publication 2), the drop in activity of the system at sub-molar levels has prevented investigators from defining reactivity in extremely dilute solutions. In the absence of such predictive models, the effect of increasing pH, Ti (III), or the temperature of the system will have to be empirically determined.

CONCLUSIONS AND RECOMMENDATIONS

The literature search identified and laboratory test confirmed that trivalent titanium components were suitable for reducing AP contaminants on equipment and building surfaces. However, these findings were not free of concerns that would attend the operation in the field. A process variable study would optimize conditions.

The initial reaction rates were quite encouraging, but as concentrations of the Ti (III) ion dropped below 400 ppm, the reaction slowed and then stopped at 180 ppm. The scope of this study did not extend to the determination of the optimization of the process variables, pH, Ti (III) concentrations, and temperature; however, sufficient data are available for the development of decontamination protocols.

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